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ORIGINAL ARTICLE

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What does an ideal wall look like?

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Abstract This paper deals with the interface between a solid and an ideal gas. The surface of the solid is considered to be an *ideal wall*, if the flux of entropy is continuous, i.e., if the interaction between wall and gas is non-dissipative. The concept of an ideal wall is discussed within the framework of kinetic theory. In particular it is shown that a non-dissipative wall must be adiabatic and does not exerts shear stresses to the gas, if the interaction of a gas atom with the wall is not influenced by the presence of other gas atoms. It follows that temperature jumps and slip will be observed at virtually all walls, although they will be negligibly small in the hydrodynamic regime (i.e., for small Knudsen numbers).

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1 Introduction

In a recent paper [1], Fried and Gurtin discussed boundary conditions in continuum theory. Based on the conservation laws and the second law of thermodynamics, they derived boundary conditions incorporating velocity slip and temperature jumps. Later in their discussion they put some emphasis on boundary conditions for non-dissipative environments, where jump and slip vanish. Below we shall show that, at least for ideal gases in contact with a solid, the only dissipation free walls are specularly reflecting walls, at which the particles are elastically reflected without changing their energy and tangential momentum. Thus, specularly reflecting walls are adiabatic and cannot transfer shear stress into the gas [2–4], and it follows that jump and slip phenomena will be present at virtually all interesting walls. However, kinetic theory shows that jump and slip are proportional to the Knudsen number [2,4], and thus jump and slip can be ignored for processes at small Knudsen numbers, in particular in the hydrodynamic regime, where the gas behavior is described by the Navier–Stokes and Fourier laws. In general settings jump and slip cannot be ignored, and the thermodynamically consistent boundary conditions of Ref. [1] must be used.

For completeness, before we begin the discussion, we point the readers' attention to classical references on jump and slip boundary conditions that were not mentioned in [1], namely the seminal paper by Waldmann [5], and the detailed discussions by Bedeaux et al. [6] and Bedeaux [7].

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The interface between two bodies is considered to be an ideal wall, if the entropy flux is continuous at the interface, i.e., the wall is non-dissipative and non-adiabatic [8]. The concept of an ideal wall was recently used to define the temperature of an ideal gas in non-equilibrium [9,10].

In the following, we consider the interface between a monatomic ideal gas and a conventional solid body [2] and ask for the properties that the surface of the solid should have in order to form an ideal wall as defined above. In kinetic theory the surface properties are modeled by an interaction probability K so that we ask for a function K corresponding to ideal walls. Cercignani shows that there will always be a production of entropy unless K is a δ-function, as long as K is independent of the phase density of the gas [2].

We shall discuss the general concept of an ideal wall and give a small extension to Cercignani's proof which leads to the conclusion that the gas particles must be reflected specularly at a non-dissipative wall. A specularly reflecting wall is adiabatic and cannot exert shear stresses to the gas [4]. Thus, kinetic theory shows that a non-dissipative wall is necessarily adiabatic, that is an ideal wall as defined above cannot exist (in contradiction to the assumptions in [9]). For small Knudsen numbers, jump and slip can be ignored, however, so that the solid-gas interface for a gas at small Knudsen numbers can be *approximated* as an ideal wall.

Only if the interaction probability K depends on the phase density of the gas, one may have a non-adiabatic ideal wall. In this case, however, the collision between the wall and a single gas atom would be influenced considerably by the presence of the other gas particles. In our opinion, this assumption is extremely unrealistic; in particular in rarefied gases the collisions of the individual gas particles with the wall should be independent of other gas particles.

The paper is organized as follows: In the next section we present the expression for the entropy production at the walls. It is an obvious consequence of this formula that the entropy production at the wall vanishes in thermodynamical equilibrium and for specular reflection. In Sect. 3 we introduce the microscopic boundary conditions and show, relying on the proof by Cercignani [2], that the entropy production is strictly positive in non-equilibrium situations unless the wall is specularly reflecting. The paper closes with a discussion of these findings with respect to small deviations from equilibrium.

2 Entropy production at the wall

For the description of the solid only three quantities are required in the present context: its temperature at the surface T_W, the non-convective energy flux q_k and the non-convective entropy flux φ_k, which is related to the two other quantities by (see, e.g., [8])

$$\varphi_k = \frac{q_k}{T_W}. \tag{1}$$

Moreover, n_i denotes the components of the unit normal vector of the wall which points into the gas.

The state of the gas at the wall is given by the phase density f, defined such that $f d\mathbf{c}$ gives the number density of particles in the velocity space element $d\mathbf{c}$ [2,4]. Throughout our discussion we shall consider all quantities of the gas in that frame of reference where the wall is at rest. Thus, c_i is the microscopic velocity of the gas particles in this particular frame.

Energy flux Q_k and entropy flux ϕ_k of the gas are given by (see, e.g., [4])

$$Q_k = \frac{m}{2}\int c^2 c_k f d\mathbf{c}, \quad \phi_k = -k\int c_k f \ln\frac{f}{y} d\mathbf{c}, \tag{2}$$

where m is the mass of a particle, k is Boltzmann's constant and $1/y$ is the size of a cell of phase space. The integration is performed over the whole space of microscopic velocity $\mathbf{c}$.

On a microscopic scale, the wall is not smooth and gas particles may move into the solid so that the interactions between gas and solid take place in a thin layer. The description of the solid inside this layer must take account for the movement of the solid's atoms and would be very complicated. Indeed, the description of the solid by the usual continuum mechanics is appropriate only outside this layer. The thickness of the layer is of the order of the maximum penetration depth which is assumed to be much smaller than the mean free path of the gas and may be ignored in comparison to the latter. It follows that the interface between gas and solid may be described as a singular surface.

While inside the two bodies—gas and solid—all fields are continuous, discontinuities may appear at the interface. In particular it is well known that one may have temperature jumps and velocity slip at a wall [1–4]. In the following, we refer to the values of all quantities directly at the interface between gas and solid only.

Due to the first law of thermodynamics there is no production of energy at the surface and the normal part of the heat flux is continuous,

$$q_k n_k = Q_k n_k. \tag{3}$$

The entropy flux, however, must not be continuous, since there might be dissipation at the interface due to the collisions of the gas atoms with the surface. The entropy production of the surface is given by the difference between the fluxes into and out of the surface,

$$\sigma = (\phi_k - \varphi_k)\, n_k, \tag{4}$$

σ is a production per unit area. The above equations (3, 4) are reduced versions of the general interface balance laws (7.10, 7.11) of Ref. [1] and are relevant for interfaces that do not carry energy and entropy, nor allow for fluxes within the interface. This is appropriate in kinetic theory as long as the Knudsen layer [2] is resolved, since then no physical interface exists. Within a macroscopic theory, where the Knudsen number is small and the Knudsen layer (which is of the order of a mean free path) cannot be resolved, the Knudsen layer is the prototype of an interface that can carry thermodynamic properties, and allows for fluxes [5].

Due to the second law of thermodynamics the entropy production at the wall should be non-negative,

$$\sigma \geq 0. \tag{5}$$

If $\sigma = 0$ holds for a non-adiabatic wall, there is no dissipation at the surface and the wall is an ideal wall.

We proceed with the calculation of σ. With (1),(2) and (3), we find

$$\sigma = \left(\phi_k - \frac{Q_k}{T_W}\right) n_k = -k \int c_k n_k f \left[\ln \frac{f}{y} + \frac{mc^2}{2kT_W}\right] d\mathbf{c}. \tag{6}$$

Here, we introduce the Maxwellian at surface temperature T_W and density ϱ_W,

$$f_W = \frac{\varrho_W}{m} \sqrt{\frac{m}{2\pi k T_W}}^3 \exp\left\{-\frac{mc^2}{2kT_W}\right\}, \tag{7}$$

which allows us to write

$$\sigma = -k \int c_k n_k f \ln \frac{f}{f_W} d\mathbf{c}, \tag{8}$$

where we have used that the flux of particles through the wall vanishes,

$$0 = \int c_k n_k f d\mathbf{c}. \tag{9}$$

From (8) follows immediately that the entropy production σ vanishes, if the gas is in equilibrium with itself—so that its phase density is a Maxwellian—and with the wall—so that its temperature is equal to T_W. This is a reflection of the so-called zeroth law of thermodynamics, which states that two bodies in equilibrium with each other (and themselves) have the same temperature, which here is the wall temperature T_W. This is a trivial case, of course, where the heat flux vanishes, and independent of the properties of the wall.

By splitting σ into two parts, accounting for incoming and leaving particles, respectively, we obtain

$$\sigma = -k \int\limits_{c_k n_k \leq 0} c_k n_k f \ln \frac{f}{f_W} d\mathbf{c} - k \int\limits_{c_k n_k \geq 0} c_k n_k f^{(+)} \ln \frac{f^{(+)}}{f_W} d\mathbf{c}, \tag{10}$$

where we have added the superscript $^{(+)}$ to the phase density for the leaving particles. Next, we substitute in the first integral $c_k \to c_k - 2c_i n_i n_k$, so that

$$\sigma = k \int\limits_{c_k n_k \geq 0} c_k n_k \left[f\left(c_k - 2c_i n_i n_k\right) \ln \frac{f\left(c_k - 2c_i n_i n_k\right)}{f_W} - f^{(+)} \ln \frac{f^{(+)}}{f_W} \right] d\mathbf{c}; \tag{11}$$

the Maxwellian is not changed by the substitution. It is obvious that σ will vanish for *any* incoming f, if

$$f^{(+)}(c_k) = f\left(c_k - 2c_i n_i n_k\right), \quad c_k n_k \geq 0. \tag{12}$$

This is the phase density for a specularly reflecting boundary which therefore forms a non-dissipative wall. However, also this case is rather trivial, since such a wall is adiabatic, i.e., $Q_k n_k = 0$.

3 Microscopic boundary conditions and entropy production

Now we consider the microscopic properties of the wall in more detail. The phase density of the particles leaving the wall ($c_k n_k \geq 0$) is determined by the phase density of the incoming particles and the microscopic properties of the surface. Following [2] we write

$$c_k n_k f^{(+)}(c_k) = - \int\limits_{c_k' n_k \leq 0} \mathcal{K}\left(c_k' \to c_k\right) c_k' n_k f\left(c_k'\right) d\mathbf{c}', \quad c_k n_k \geq 0, \tag{13}$$

where the kernel $\mathcal{K}\left(c_k' \to c_k\right)$ gives the probability that a particle hitting the wall with velocities around c_k' will leave the wall with velocities around c_k. Equation (13) is appropriate when adsorption of the particles at the wall may be ignored, see [2] for discussion. The kernel does not depend on the phase density, due to the assumption that the collision probability for a single gas particle is not affected by the presence of other gas particles.

Since the wall does not accumulate particles, the total probability that a particle leaves the wall is unity, i.e.,

$$\int\limits_{c_k n_k \geq 0} \mathcal{K}\left(c_k' \to c_k\right) d\mathbf{c} = 1, \quad c_k' n_k \leq 0. \tag{14}$$

This equation guarantees that condition (9) is fulfilled. Moreover, the kernel must be chosen such that equilibrium between gas and solid, once reached, will last. Hence, the wall Maxwellian f_W must fulfill the boundary condition (13), i.e.,

$$c_k n_k f_W(c_k) = - \int\limits_{c_k' n_k \leq 0} \mathcal{K}\left(c_k' \to c_k\right) c_k' n_k f_W\left(c_k'\right) d\mathbf{c}', \quad c_k n_k \geq 0. \tag{15}$$

The simplest non-trivial model which fulfills all criteria on the boundary conditions was given by Maxwell [2–4]. For Maxwell boundary conditions one assumes that a fraction $(1-\alpha)$ of the emerging particles is specularly reflected while the remaining part α leaves the wall distributed according to the wall Maxwellian f_W. Here, α is the accommodation coefficient; temperature jump and slip depend on α and the Knudsen number.

For any probability density $\mathcal{K}\left(c_k' \to c_k\right)$ which fulfills the criteria given in this section, Cercignani proves that σ given by (8) is non-negative, see his book [2] for details of the ingenious proof. In particular the proof implies that σ will vanish if $f = f_W$, i.e., in the equilibrium case, see the discussion above, or if

$$-\mathcal{K}\left(c_k' \to c_k\right) \frac{c_k' n_k f_W\left(c_k'\right)}{c_k n_k f_W(c_k)} = \delta\left(c_k' - c_k^*\right), \quad c_k' n_k \leq 0, \quad c_k n_k \geq 0, \tag{16}$$

where c_k^* "can be any function of c_k provided Eq. (14) is satisfied" [2]. Note, that $c_k^* n_k \leq 0$ must hold for $c_k n_k \geq 0$.

According to this result the interaction between gas and wall is deterministic: Consider a beam of gas particles all traveling towards the wall with the same velocity c_i^*. After collision with the wall, all particles of the beam will have the velocity c_k so that there is a beam also after collision. Due to the microscopic structure of a real wall, however, one expects that the collisions will destroy the beam structure: after collision the beam should fan out, which implies dissipation, i.e., entropy generation.

With (16) the question for an ideal wall is reduced to finding an appropriate function $c_k^*(c_i)$. In extension to Cercignani's proof, we shall show now that there is only one choice for $c_k^*(c_i)$, namely the specularly reflecting wall. For the proof we insert the kernel (16) into (13) to obtain

$$f^{(+)}(c_k) = \frac{f_W(c_k)}{f_W\left(c_k^*\right)} f\left(c_k^*\right) = e^{\frac{m}{2kT_W}\left(c^{*2} - c^2\right)} f\left(c_k^*\right), \quad c_k n_k \geq 0, \quad c_k^* n_k \leq 0. \tag{17}$$

$f\left(c_k^*\right)$ on the right-hand side of (17) denotes the phase density of particles flying towards the wall, evaluated at c_k^*. As we have said, the function $c_k^*(c_i)$ must be chosen so that (14) is satisfied, which is equivalent to (9). With (17) the latter may be written as

$$0 = \int\limits_{c_k n_k \geq 0} c_k n_k \left[e^{\frac{m}{2kT_W}\left(c^{*2} - c^2\right)} f\left(c_k^*\right) - f\left(c_k - 2c_i n_i n_k\right) \right] d\mathbf{c}, \tag{18}$$

where f is the phase density of incoming particles in both terms. We have assumed that the wall–gas interactions are independent of the phase density. Thus, $c_k^*(c_i)$ is a property of the surface and independent of the phase density. It follows that Eq. (18) must hold for arbitrary functions $f(\cdot)$. Accordingly the integrand in (18) has to vanish for *all* f, which implies that

$$c_k^* = c_k - 2c_i n_i n_k. \tag{19}$$

Accordingly, the kernel (16) may be written as

$$\mathcal{K}\left(c_k' \to c_k\right) = \delta\left(c_k' - (c_k - 2c_i n_i n_k)\right). \tag{20}$$

Here we have derived, again, the condition for the specularly reflecting wall. In particular, the kernel (20) does not change the energy of the colliding particles; thus, the wall is adiabatic, nor does it change the momentum parallel to the wall; thus, the wall exerts no shear stresses to the gas.

It is instructive to discuss the origin of the entropy production at the wall which is directly related to the probabilistic nature of the boundary condition (13): Consider a particle of velocity c_k' approaching the wall. After collision with the wall, the particle will have the velocity c_k'' with the probability $\mathcal{K}\left(c_k' \to c_k''\right)$. Now, if after collision the velocity is inverted, $c_k'' \to -c_k''$, the particle undergoes a new collision after which it will have the velocity $-c_k'''$ with probability $\mathcal{K}\left(-c_k'' \to -c_k'''\right)$. In most cases the particle does not return on its original trajectory, i.e., c_k''' will generally differ from c_k', and thus the process is irreversible and entropy is produced, $\sigma \geq 0$. For the specularly reflecting wall, however, where the kernel is given by (20),

$$\mathcal{K}\left(c_k' \to c_k''\right)\mathcal{K}\left(-c_k'' \to -c_k'''\right) = \delta\left(c_k' - c_k'''\right)$$

holds, which means that the particle will return on its original trajectory. Then, the process is reversible and there is no production of entropy, $\sigma = 0$.

4 Discussion

A deterministic or a specularly reflecting wall will never be met in nature. Thus, the entropy production at physically relevant walls will be strictly positive (i.e., non-zero!) in non-equilibrium. We ask what this means for the boundary conditions for temperature and velocity.

First, we consider processes where the deviation from equilibrium is small. The corresponding smallness parameter in kinetic theory is the Knudsen number Kn, defined as the ratio between the mean free path l of the gas and a typical macroscopic length L of the process under consideration, $\mathrm{Kn} = l/L$. For small values of the Knudsen number, $\mathrm{Kn} \ll 1$, the Navier–Stokes–Fourier equations are appropriate for the description of the gas. These follow from the Chapman–Enskog method [2–4] which gives the phase density as $f_M(1 + \mathrm{Kn}\Psi)$, where f_M denotes the local Maxwellian. Then, the gas is very close to equilibrium with the wall and both, temperature jump and velocity slip between wall and gas, are proportional to the Knudsen number; the detailed calculations for Maxwell-type boundary conditions can be found for instance in Refs. [3,4]. The corresponding entropy production is proportional to Kn^2. Its computation from (10) follows along the same lines; however, this fairly technical exercise is not presented here.

In the limit of small Knudsen numbers, one may ignore the jumps, so that temperature and velocity are *assumed* to be continuous. Thus, in the Navier–Stokes–Fourier equations, one may use temperature and velocity of the wall as boundary conditions for temperature and velocity of the gas, or, alternatively, one might describe heat flux or stress at the wall, see the discussion in [1]. These are the typical boundary conditions for the Navier–Stokes–Fourier equations, and they correspond to vanishing entropy production at the wall. In other words: In the limit of small Knudsen numbers, the entropy production σ at the gas–wall interface can be ignored, so that *all* walls *appear* to be ideal, but they are not.

We turn our attention to processes far from equilibrium, in rarefied gases, where the Knudsen number is not small. Accordingly, the entropy production cannot be ignored and one has to expect discontinuities in temperature and velocity, i.e., jump and slip, between solid and gas. These depend on the details of the kernel $K\left(c_k' \to c_k\right)$; explicit calculations for Maxwell boundary conditions can be found in [3,4,11].

Note that for rarefied gases, the temperature jump and the velocity slip are followed by marked boundary layers, known as Knudsen layers, which are of the width of the mean free path l [2,4,12]. In the hydrodynamic regime, where Kn is small, the Knudsen layers are narrow, and are often incorporated into jump and slip by means of the Knudsen layer correction [2].

All the above is true as long as the interaction between gas and surface is modeled by an interaction probability $K\left(c_k' \to c_k\right)$ as in Sect. 3. In [9,10], however, the authors treat the boundary value problem for the temperature in stationary heat transfer in a different manner. They assume that the state of the gas for larger Knudsen numbers is sufficiently described by the so-called maximum entropy phase density for 14 moments. Furthermore they demand that the wall is non-dissipative and non-adiabatic, i.e., ideal. The values of the moments at the interface are adjusted in order to let the entropy production vanish. Accordingly, heat flux *and* entropy flux are continuous at the wall, and the same is true for the thermodynamic temperature which was defined in [9,10]. In this approach, no reference to the features of the surface is needed. The phase densities for incoming and leaving particles are determined by the same parameters, i.e., the moments. Unfortunately, this approach finds no support in the kinetic theory of gases since the microscopic boundary conditions of kinetic theory (13) lead to a non-vanishing entropy production, unless the wall is specularly reflecting.

Therefore, in the ideal wall approach of [9,10], the relation between the phase densities of incoming and outgoing particles cannot be given by a simple relation as (13), but must be more complicated in order to ensure vanishing entropy production. It is not clear whether it even would be possible to determine the corresponding interaction law between gas particles and the surface, but it is obvious that now the interaction law must depend on the phase density of the gas.

Speaking about gases, this seems to be unrealistic. The mean distances between particles are much larger than the interaction radii, and there is no reason to assume an influence of other gas particles to the interaction of a single particle with the wall. It should be noted that for the same reason only binary collisions are taken into account in the Boltzmann equation. Indeed, the Ansatz (13) may be considered as the equivalent to Boltzmann's *Stosszahlansatz* for the gas–wall interaction.

Obviously, the discussion would be more complicated when the boundary conditions for liquids are concerned. Nevertheless, we believe that one cannot expect to find an ideal wall, i.e., a non-dissipative non-adiabatic wall, in physical reality. This implies that temperature jumps and slip will be present at virtually all walls, although they will be negligibly small in many cases (e.g., for gases at small Knudsen numbers, or for liquids).

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